

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 20 AUG 2004

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Applicant's or agent's file reference LU6010/CB	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/03562	International filing date (day/month/year) 05.04.2003	Priority date (day/month/year) 10.04.2002
International Patent Classification (IPC) or both national classification and IPC C07C13/465		
Applicant BASELL POLYOLEFINE GMBH		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 4 sheets.

- This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 18.09.2003	Date of completion of this report 23.08.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer O'Sullivan, P Telephone No. +31 70 340-4511 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP 03/03562

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-15 as originally filed

Claims, Numbers

1-9 received on 27.07.2004 with letter of 27.04.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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International application No. **PCT/EP 03/03562**

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-9
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-9
Industrial applicability (IA)	Yes: Claims	1-9
	No: Claims	

2. Citations and explanations

see separate sheet

Re: Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1: WO 00/07968 A (BOULDER SCIENT CO ;BARNES HAMLIN H (US); SULLIVAN JEFFREY M (US)) 17 February 2000 (2000-02-17)
- D2: US-A-5 278 264 (ANTBERG MARTIN ET AL) 11 January 1994 (1994-01-11)
- D3: PATENT ABSTRACTS OF JAPAN vol. 018, no. 511 (C-1253), 27 September 1994 (1994-09-27) -& JP 06 172433 A (MITSUBISHI PETROCHEM CO LTD), 21 June 1994 (1994-06-21)
- D4: DATABASE CROSSFIRE BEILSTEIN [Online] Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; XP002251877 Database accession no. 5806372
- D5 : M Adamczyk et al, J. Org. Chem., 1984, 49, 4226-4237

Novelty (Art 33(2) PCT)

D5 discloses a process for the production of *alkyl*-substituted indenenes (see D9, page 4233, "General procedure for the preparation of 4-alkylindans 12 from 7-bromo-1*H*-indene"). In D5, 7-methyl-1*H*-indene was synthesised by reaction of 7-bromo-1*H*-indene with methylmagnesium bromide in the presence of [Ni(dppp)₂]Cl in ether. The same procedure was applied in the preparation of 5-Alkylindenenes (page 4233, bottom of col. 2). The difference between the present application and D9 is the use of chloro-indenenes in the former compared to bromo-indenenes in the latter as starting material. Claims 1-5 therefore fulfill the requirements of Art 33(2) PCT.

The compounds of claim 6 are new. Claims 6-9 therefore fulfill the requirements of Art 33(2) PCT.

Inventive Step (Art 33(2) PCT)

D5 is considered to be the closet prior art as it discloses a process for the production of *alkyl*-substituted indenenes (see D9, page 4233, "General procedure for the preparation of 4-alkylindans 12 from 7-bromo-1*H*-indene"). In D5, 7-methyl-1*H*-indene was synthesised by reaction of 7-bromo-1*H*-indene with methylmagnesium bromide in the presence of [Ni(dppp)₂]Cl in ether. The same procedure was applied in the preparation of 5-Alkylindenenes (page 4233, bottom of col. 2). The difference between the present application and D5 is the use of chloro-indenenes in the former compared to bromo-

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/03562

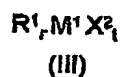
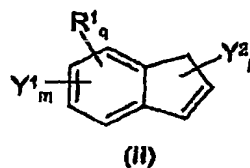
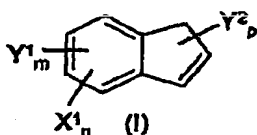
indenes in the latter as starting material as well as the presence of a substituent on the five-membered ring in the former. The effect of the difference is that the use of comparatively expensive bromoindenes is avoided. The problem can therefore be formulated as the provision of a process to produce alkylindenes where expensive bromoindenes are avoided. The solution is the use of chloro-indenes. This solution cannot be considered inventive because the skilled man faced with the problem would, given his knowledge of D5, have tried the cheaper chloro-indene in the same reaction with expectation of success. The skilled man is highly aware of the Grignard reaction in general and the theory that Mg will insert into a C-halogen bond (more specifically C-Br or C-Cl). That the bromoindene was used as starting material in D5 cannot be considered to teach away from the invention since the syntheses involved in D5 are small scale and the cost of the starting materials was unlikely to have held any importance. Claim 1-5 are therefore not considered inventive.

Claims 6-9 concern particular indene compounds and their use for the synthesis of metallocene complexes for the polymerisation of olefins. D1 discloses (examples 6 and 7) the compound 7-(1-naphthyl)indene and its use in the production of metallocene catalysts for use in olefin polymerisation reactions. The structural difference between the compound of example 6, D1 and the compounds of the present application, claim 6, lies only in the presence of a CH_2 group separating the naphthyl group from the indene ring in the latter. No apparent advantage is attributable to this difference. Therefore the problem to be solved by the compounds of claim 6 and use claims 7-9 may be formulated as the provision of alternative compounds for the given use. The skilled man would, with expectation of success, have made the structural changes to the compound of D1 to solve said problem. Claims 6-9 are therefore not considered inventive.

no set of claims (July 2004)

We claim:

1. A process for preparing indenenes of the formula (II) from indenenes of the formula (I) by reaction with compounds of the formula (III).



where

X^1 is chlorine;

Y^1 is C_1 - C_{10} -alkyl, C_6 - C_{10} -aryl or C_7 - C_{14} -alkylaryl;

Y^2 is C_1 - C_{10} -alkyl, C_6 - C_{10} -aryl or C_7 - C_{14} -alkylaryl, and Y^2 is a substituent in position 2 of the indene skeleton;

R^1 are identical or different and are selected independently from the group consisting of linear, branched or cyclic aliphatic hydrocarbon groups, e.g. C_1 - C_{25} -alkyl which may in turn bear a variety of substituents, and groups bound via an aliphatic group to the indenyl skeleton, e.g. C_3 - C_{15} -alkenylalkyl, C_3 - C_{15} -alkynylalkyl, C_5 - C_{24} -heteroarylalkyl, C_7 - C_{30} -arylalkyl, C_2 - C_{30} -alkyloxyalkyl, C_7 - C_{30} -aryloxyalkyl, C_8 - C_{30} -alkylarylalkyl, and other heteroatom-containing groups which are bound via an aliphatic group to the indenyl skeleton, e.g. boron-, silicon-, nitrogen-, oxygen- or sulfur-containing groups, and may bear one or more substituents;

M^1 is Mg;

X^2 are identical or different and are halogen atoms;

m is 0 to 1;

n is 1 to 2;

p is 1;

q is 1 or 2;

r is 1, 2 or 3, and

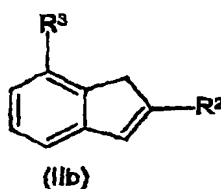
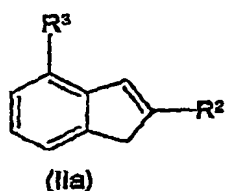
t is 0, 1 or 2, where $r + t$ corresponds to the oxidation number of M^1 ;

wherein the indenenes of the formula (I) are reacted with appropriate aliphatic organometallic compounds of the formula (III) in the presence of a complex of nickel.

2. A process as claimed in claim 1, wherein a complex of nickel selected from the group consisting of nickel(II) acetylacetonate, [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride, [1,1'-bis(diphenylphosphino)ferrocene]nickel(II) chloride, bis(tributylphosphine)nickel(II) bromide, bis(tributylphosphine)nickel(II) chloride, bis(triphenylphosphine)nickel(II) chloride, bis(triphenylphosphine)dicarbonylnickel(0), [1,2-bis(dimethylphosphino)ethane]nickel(II) chloride, bis(triethylphosphine)nickel(II) chloride and the [1,1'-bis(diphenylphosphino)ferrocene]nickel(II) chloride-methylene chloride complex is used.

3. A process as claimed in claim 1 or 2, wherein the complex of nickel used is [1,3-bis(diphenylphosphino)propane]nickel(II) chloride.
4. A process as claimed in any of claims 1-3, wherein the transition metal catalyst is added in an amount of from 0.01 to 5 mol%, based on chloroindene of the formula (I) used.
5. A process as claimed in any of claims 1-4, wherein the chloroindenes of the formula (I) which are used are selected from the groups consisting of:
2-methyl-4-chloro-1-indene; 2,7-dimethyl-4-chloro-1-indene; 2,4-dimethyl-7-chloro-1-indene; 2-methyl-5-chloro-1-indene; 2-methyl-6-chloro-1-indene; 2-methyl-7-chloro-1-indene; 2-ethyl-4-chloro-1-indene; 2-ethyl-5-chloro-1-indene; 2-ethyl-6-chloro-1-indene; 2-ethyl-7-chloro-1-indene; 2-propyl-4-chloro-1-indene; 2-propyl-5-chloro-1-indene; 2-propyl-6-chloro-1-indene; 2-propyl-7-chloro-1-indene; 2-i-propyl-4-chloro-1-indene; 2-i-propyl-5-chloro-1-indene; 2-i-propyl-6-chloro-1-indene; 2-i-propyl-7-chloro-1-indene; 2-butyl-4-chloro-1-indene; 2-butyl-5-chloro-1-indene; 2-butyl-6-chloro-1-indene; 2-butyl-7-chloro-1-indene; 2-s-butyl-4-chloro-1-indene; 2-s-butyl-5-chloro-1-indene; 2-s-butyl-6-chloro-1-indene; 2-s-butyl-7-chloro-1-indene; 2-t-butyl-4-chloro-1-indene; 2-t-butyl-5-chloro-1-indene; 2-t-butyl-6-chloroindene; 2-t-butyl-7-chloroindene.

6. An indene of the formula (IIa) or (IIb),



where

R^2 is C_1 - C_{10} -alkyl and

R^3 is a monocyclic or polycyclic C_5 - C_{15} -alkyl group or a CH_2R^4 group,

where

R^4 is a C_6 - C_{14} -aryl group, a C_7 - C_{16} -alkylaryl group or a monocyclic or polycyclic C_5 - C_{15} -alkyl group.

7. The use of indenenes of the formula (IIa) or (IIb) as claimed in claim 6 for the synthesis of metallocene complexes.

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8. An ansa-bisindenylmetallocene prepared from at least one indene of the formula (IIa) or (IIb) as claimed in claim 6, wherein the two indenyl ligands of the metallocene have different substituents in the 2 position.
9. The use of at least one ansa-bisindenylmetallocene as claimed in claim 8 for the polymerization of olefins.